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PIEZO-OPTIC PROPERTIES OF LIQUIDS UNDER HIGH PRESSURE

Annual Summary Report

Contract No. N00014-75-C-0915; NR381-018

Physics Program, Code 421
Office of Naval Research
Arlington, Virginia 22217

December 15, 1976

K. Vedam

THE MATERIALS RESEARCH LABORATORY

THE PENNSYLVANIA STATE UNIVERSITY

UNIVERSITY PARK, PENNSYLVANIA

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20. ABSTRACT (*Continue on reverse side if necessary and identify by block number*)

A high pressure liquid cell interferometer to measure the variation of refractive index of liquids with pressure to 14 kbars is described. The amount of liquid needed is only 3 c.c. Interferometric measurements on a number of liquids at high pressure show (i) first experimental proof that the Eulerian frame-indifferent analogue strain E is a more useful strain measure than the Lagrangian strain, (ii) Keane's equation of state best describes each and all liquids stuided, (iii) change in refractive index vs

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E is linear for all liquids, even though the volume strain involved is as high as 33%.

1. INTRODUCTION

On May 1, 1975 a new program was initiated under the sponsorship of the Office of Naval Research (Physics Program) to carry out a systematic study on the piezo-optic properties of liquids under high pressure. Since then significant progress has been made in this program and in what follows, a brief summary of the work accomplished to date is presented.

2. WORK ACCOMPLISHED

The technique of high pressure-optical interferometry which has been developed and successfully employed by the author and his students for studies on the piezo-optic properties of solids, has now been adapted for similar studies on liquids. Measurements on the variation of the refractive indices of a number of liquids at room temperature have been completed. The results obtained have already been communicated in the form of two short articles to Physical Review Letters and another to Review of Scientific Instruments. One of the Physical Review Letters was also submitted to ONR as part of the Technical Report No. 1, dated December 22, 1975. Copies of the other two articles are attached as appendices to this proposal. Hence, in what follows only some of their highlights are mentioned and wherever the description in any of the articles is too brief, additional data and discussion thereof are presented here.

In brief it has been possible to carry out the optical interferometric measurements with a number of liquids such as water, CCl_4, chlorobenzene, n-pentane, n-hexane, n-heptane, n-octane, n-nonane, and n-decane, right up to their high pressure-freezing points or 14 kbars or whichever is lower. In all cases the refractive indices of the liquids were found to increase with pressure with pronounced nonlinearity. However, this nonlinearity is very

much reduced when Δn, the change in refractive index, is plotted as a function of the Lagrangian strain η. In the case of solids it was found that the change in refractive index was exactly linear with Lagrangian strain in the entire range of pressures investigated. But in these liquids, at low pressures when η is small, Δn vs. η is linear but becomes nonlinear at high pressure. Such a nonlinearity can arise from one or more of the following causes: (i) unreliable P-V data used to evaluate η; (ii) instead of Lagrangian strain η, the Eulerian strain or some other representation of strain should be used; (iii) wrong equation of state of liquids used; (iv) intrinsic nonlinearity. In order to narrow down these alternatives, all these piezo-optic data on all the liquids were analyzed by least squares technique using all the published P-V data and the various equations of state widely used in the literature. Table I lists the different Equations of State considered in this work. Similarly for every liquid studied all the published P-V data were also considered in the analysis.

Firstly, such an analysis was helpful in eliminating some P-V data as not being sufficiently accurate or reliable. Further, we found in every case the range of linearity between Δn and strain is much larger when the strain is evaluated in the Eulerian frame of reference than with the Lagrangian representation, regardless of the type of equation of state used. Therefore, E (= ε) appears to be a more useful strain measure than η. Identical conclusions on the usefulness of E over η were deduced by Davies[1] from the data on pressure dependence of the elastic moduli as well as the Hugoniot data on MgO.

Tables II-V compare the degree of the fit of Δn, to various degrees of polynominals in E, for water, CCl_4, n-octane and chlorobenzene, respectively. for a number of equations of state discussed in the literature. It is seen that a linear relation between Δn and E is obtained with 2nd-Order Murnaghan equation as evidenced by the minimum value of the sum of the squares of residuals as well as the standard error. The 2nd-Order Birch, Tait and Keane equations also give essentially similar results, whereas other equations such as Bridgman, 1st-Order Birch (also called Birch-Murnaghan equation), and 1st-Order Murnaghan equations give poor fits unless one uses higher order polynomials. The results on other liquids are similar and hence are not reported here.

As Anderson[2], Chhabildas and Ruoff[3] have shown that, of all the equations of state reported in the literature only Keane's equation yields physically as well as thermodynamically meaningful values on extrapolation to very high

Table I. Nonlinear Equations of State

Equation Name	Acronym	Form
Tait	TE	$x = [\exp\{(1 - y)(1 + m)\} - 1]\,(1 + m)^{-1}$
Linear Secant-Modulus	LSME	$x = (1 - y)[1 - \frac{1}{2}(1 - y)(1 + m)]^{-1}$
1st-Order Murnaghan	ME_1	$x = m^{-1}(y^{-m} - 1)$
2nd-Order Murnaghan	ME_2	$x = 2m^{-1}[y^{-nm} - 1][(n - 1)y^{-nm} + (n + 1)]^{-1}$
1st-Order Birch	BE_1	$x = \frac{3}{2}y^{-5/3}[b_1(y^{-2/3} - 1) + b_2(y^{-2/3} - 1)^2]$
2nd-Order Birch	BE_2	$x = \frac{3}{2}y^{-5/3}[b_1(y^{-2/3} - 1) + b_2(y^{-2/3} - 1)^2 + b_3(y^{-2/3} - 1)^3]$
Keane	KE	$x = \frac{B_o'}{(B_\infty')^2}[y^{-B_\infty'} - 1] + \frac{(B_o' - B_\infty')}{B_\infty'} \ln y$

where $x = p/B_o$, $y = V/V_o$, $m = B_o'$, $n = [1 - 2B_oB_o''/(B_o')^2]^{1/2}$

$b_1 = 1$, $b_2 = \frac{3}{4}(B_o' - 4)$, $b_3 = \frac{1}{24}[143 + 9(B_o' - 7)B_o' + 9B_oB_o'']$

$B_\infty' = B_o' + B_oB_o''/B_o'$

Table II. Least-Squares Fitting Results for Water Using Adams P-V Data to Compute E; Δn Measured at 25°C Using λ5893Å.

Equation	$\Delta n = AE + BE^2 + CE^3$			Sum of Squares of Residuals	Standard Error
	A	B	C		
Tait	-0.985			12.75×10^{-7}	1.47×10^{-4}
	-0.979	0.100		9.16	1.26
	-0.964	0.674	4.959	5.83	1.01
1st-Order Murnaghan	-0.986			9.04×10^{-7}	1.24×10^{-4}
	-0.980	-0.088		6.26	1.04
	-0.991	-0.338	-3.685	4.42	0.88
2nd-Order Murnaghan	-0.986			7.83×10^{-7}	1.15×10^{-4}
	-0.979	-0.094		4.70	0.90
	-0.976	0.227	1.153	4.52	0.89
1st-Order Birch	-0.985			18.36×10^{-7}	1.76×10^{-4}
	-0.979	-0.097		14.98	1.60
	-0.956	0.952	7.384	7.59	1.15
2nd-Order Birch	-0.986			8.64×10^{-7}	1.21×10^{-4}
	-0.979	0.096		5.38	0.96
	-0.977	0.180	0.727	5.31	0.96
Keane	-0.986			9.01×10^{-7}	1.23×10^{-4}
	-0.979	0.096		5.71	0.99
	-0.977	0.181	0.731	5.64	0.99

Table III. Least-Squares Fitting Results for CCl_4 Using Mopsik P-V Data to Compute E; Δn Measured at 25°C Using λ5893Å.

Equation	$\Delta n = AE + BE^2 + CE^3$			Sum of Squares of Residuals	Standard Error
	A	B	C		
Tait	-1.486			11.84×10^{-7}	1.76×10^{-4}
	-1.476	0.343		10.63	1.69
	-1.532	-4.929	-1.079×10^2	2.41	0.82
1st-Order Murnaghan	-1.487			16.00×10^{-7}	2.05×10^{-4}
	-1.475	0.431		14.08	1.95
	-1.541	-5.800	-1.276×10^2	2.60	0.85
2nd-Order Murnaghan	-1.476			3.55×10^{-7}	0.97×10^{-4}
	-1.487	-0.374		2.10	0.75
	-1.474	0.808	24.217	1.69	0.68
1st-Order Birch	-1.483			4.25×10^{-7}	1.06×10^{-4}
	-1.478	0.164		3.97	1.04
	-1.506	-2.539	- 55.345	1.81	0.71
2nd-Order Birch	-1.479			1.55×10^{-7}	0.64×10^{-4}
	-1.482	-0.112		1.42	0.62
	-1.480	0.044	3.190	1.41	0.62
Keane	-1.479			1.50×10^{-7}	0.63×10^{-4}
	-1.481	-0.087		1.42	0.62
	-1.481	-0.043	0.896	1.42	0.63

Table IV. Least-Squares Fitting Results for n-Octane Using Eduljee P-V Data to Compute E; Δn Measured at 25°C Using λ5893Å.

Equation	$\Delta n = AE + BE^2 + CE^3$			Sum of Squares of Residuals	Standard Error
	A	B	C		
Tait	-1.332			27.53×10^{-7}	2.53×10^{-4}
	-1.332	0.005		27.53	2.56
	-1.360	-1.230	-11.760	16.00	1.97
1st-Order Murnaghan	-1.335			98.49×10^{-7}	4.78×10^{-4}
	-1.348	-0.208		88.25	4.58
	-1.415	-3.186	-28.354	21.25	2.28
2nd-Order Murnaghan	-1.332			32.43×10^{-7}	2.75×10^{-4}
	-1.333	-0.016		32.37	2.78
	-1.362	-1.278	-12.015	20.34	2.23
1st-Order Birch	-1.327			91.03×10^{-7}	4.60×10^{-4}
	-1.302	0.423		48.88	3.41
	-1.248	2.811	22.738	5.80	1.19
2nd-Order Birch	-1.332			26.21×10^{-7}	2.47×10^{-4}
	-1.331	0.013		26.17	2.49
	-1.358	-1.168	-11.250	15.62	1.95
Keane	-1.329			19.85	2.15×10^{-4}
	-1.331	-0.020		19.75	2.17
	-1.354	-1.053	- 9.835	11.69	1.69

Table V: Least-Squares Fitting Results for Chlorobenzene Using Bridgman P-V Data to Compute E; Δn Measured at 25°C Using λ5893Å

Equation	$\Delta n = AE + BE^2 + CE^3$			Sum of Squares of Residuals	Standard Error
	A	B	C		
Tait	-1.718			52.51×10^{-7}	3.58×10^{-4}
	-1.701	0.321		39.06	3.12
	-1.760	-2.508	-30.101	8.37	1.46
1st-Order Murnaghan	-1.721			11.53×10^{-6}	5.30×10^{-4}
	-1.700	0.400		9.44	4.86
	-1.798	-4.272	-49.700	1.08	1.66
2nd-Order Murnaghan	-1.712			11.98×10^{-7}	1.71×10^{-4}
	-1.707	0.104		10.57	1.63
	-1.705	0.169	0.691	10.56	1.64
1st-Order Birch	-1.714			10.29×10^{-7}	1.58×10^{-4}
	-1.700	0.253		1.91	0.69
	-1.697	0.404	1.608	1.82	0.68
2nd-Order Birch	-1.714			12.81×10^{-7}	1.77×10^{-4}
	-1.700	0.272		3.12	0.88
	-1.708	-0.110	- 4.071	2.56	0.81
Keane	-1.715			13.49×10^{-7}	1.81×10^{-4}
	-1.700	0.287		2.75	0.83
	-1.708	-0.124	- 4.372	2.11	0.73

pressures. Hence, in all further work we propose to use Keane's equation of state, instead of 2nd-Order Murnaghan, 2nd-Order Birch and Tait equations. This analysis has revealed that Keane's equation gives excellent linear fit between Δn and E for all liquids studied, irrespective of the nature of the liquid, whether polar or nonpolar and whether composed of spherically symmetric or long chain molecules. Thus, the present optical measurements support similar conclusions derived from the ultrasonic and Hugoniot measurements on solids regarding the relative validity and usefulness of these equations of state.

2.1. Publications

1. Piezo-optic Behavior of Water and Carbon Tetrachloride Under High Pressure: By K. Vedam and P. Limsuwan, Phys. Rev. Letts. 35, 1014 (1975).

2. Piezo-optic Behavior and the Equation of State of Liquids: By K. Vedam and P. Limsuwan, submitted for publication in Phys. Rev. Letts.

3. Optical Interferometry in Liquids at High Pressures to 14 Kbars: By K. Vedam and P. Limsuwan, accepted for publication in Rev. Sci. Instruments.

2.2. Oral Presentation at Scientific Meetings

Piezo-optic Behavior and the Equation of State of Liquids: By P. Limsuwan and K. Vedam, to be presented at the ensuing "Washington Area High Pressure Colloquium" at the U.S. Naval Academy, Annapolis, Maryland, October 13, 1976.

APPENDIX I

Accepted for Publication in Review of Scientific Instruments

Optical Interferometry in Liquids at High Pressures to 14 Kbars*

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University Park, Pennsylvania 16802

Optical interferometric measurements on fluids at high pressures have been reported in the literature but the maximum pressure attained in these measurements have been 2.5 kbars in the case of gases(1) and only 1.1 kbars in the case of liquids.(2) The authors have developed an interferometric system for use in liquids up to a maximum pressure of 14 kbars, and thus have been able to observe interesting nonlinear piezo-optical effects.(3)

A schematic diagram of the liquid cell interferometer is shown in Figure 1. The interferometer consists of a stainless steel container [see No. 1 in Figure 1] about 2 cm diameter and 1.8 cm long. One end of this container is connected to a polyethylene bag [7] containing the liquid [6] under study, with a Buna-N O-ring [9] providing a tight seal. The other end of the container is also sealed with another Buna-N O-ring [9] and a stainless steel cap [12]. A vitreous silica disc [13], cemented with Eastman 910 adhesive(4) to the stainless steel cap [12] acts as the optical window to the interferometer and also prevents the mixing of the experimental liquid [6] inside the interferometer with the fluid pressure medium on the outside.

The optical components of the interferometer consists of an optical flat [5], a vitreous silica plano-convex lens [3] and a vitreous silica spacer [4] between the optical flat and the lens. A small hole [8] in the base of the stainless steel container [1] as well as in the optical flat [5] allows the space between the lens and the flat to be filled with the liquid in the polyethylene bag. These components are properly aligned with the help of the three stainless steel screws [10] and the three miniature(5) spring plungers [11], so that localized Newtonian fringes can be obtained between the optical flat and the convex side of the lens with the spacer and the liquid in between. To increase the contrast of the fringes both the optical

flat and the lens were partially silvered with a thin coating of aluminum. The spacer for this interferometer was fabricated from vitreous silica but before fabrication, the large block of vitreous silica itself was used to determine its second- and third-order elastic constants. With this information and a knowledge of the pressure in the system as read by a precision Heise gauge or Manganin gauge, the exact thickness of the spacer of the interferometer at any pressure could be evaluated.

The entire interferometer assembly could be inserted into the 14 kbar high pressure optical vessel which has been already described[6] in connection with similar measurements on the variation of refractive index of alakli halides with pressure to 14 kbars. Figure 2 is a schematic diagram of the high pressure optical vessel and the experimental arrangement for measuring the variation of refractive index of liquids with pressure. Plexol 262 (di-2 ethyl hexyl adipate)[7] was used as the pressure medium. As the pressure in the system is increased, the flexibility of the polyethylene bag containing the fluid under study allows the optical interferometer to be filled with the liquid at all pressures. The maximum amount of liquid necessary for these measurements is only about 3 c.c.

A chromel-alumel thermocouple coupled to a potentiometer has also been added to the rear plug of the high pressure vessel. Since the mass of the optical pressure vessel is rather large and since the rate of compression can be adjusted and controlled to be very slow, it has been possible to maintain the thermal equilibrium at every stage to within 0.1°C and thus corrections for thermal fluctuations is not needed. For measurements at temperatures slightly warmer than ambient temperature, the entire pressure chamber can be heated by a small heating coil wrapped around it.

As the pressure in the system is increased, the refractive index of the liquid in the interferometer as well as the thickness of the spacer are altered with consequent shift of the interference fringes across a fiducial mark on the optical flat of the interferometer. The change in refractive index Δn of the liquid could be evaluated from the interference formula

$$\Delta n = (p\lambda - 2n\cdot\Delta t)/2t_0 \tag{1}$$

where p is the number of fringes shifted, Δt the change in the thickness of the vitreous silica spacer, and t_0 the initial thickness of the spacer.

Such a computational procedure implies the following two assumptions: (i) the radius of curvature of the lens does not change significantly by the change in pressure and (ii) the thickness of the spacer is the same as the true thickness of the interferometer at the fiducial mark. Since the radius of curvature of the plano-convex lens of the interferometer is very large ($\sim$ 1000 cm) and since the pressure change in any one measurement and the consequent computation involved using Equation (1), never exceeded 1000 psi, the above assumptions are considered to be valid and the consequent errors involved are considered to be negligible.

Table I presents the typical results obtained on two liquids, n-hexane and n-pentane. In the case of n-hexane the measurements had to be terminated at 11.66 kbars since it froze at this pressure at 25°C. The table gives the values of the refractive indices of the liquids at atmospheric pressures, the total number of fringes shifted and the total observed change Δn in the refractive index of the liquid. Figure 3 shows graphically the observed variation of the refractive indices of these two liquids with pressure to 14 kbars.

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*Research work supported by the Office of Naval Research, Physics Program.

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3. K. Vedam and P. Limsuwan, Phys. Rev. Letts., 35, 1014 (1975); 38 (1977). (to be published).
4. Manufactured by Eastman Kodak Company.
5. Available from Manhattan Supply Co., Ames Court, Engineers Hill, Plainview, Long Island, New York 11803.
6. K. Vedam, E. D. D. Schmidt, J. L. Kirk and W. C. Schneider, Mat. Res. Bull., 4, 573 (1969).
7. Available from Rohm and Haas Co., Philadelphia, Pa.

Table I. Variation of the Refractive Index of Liquids with Pressure at $\lambda 5461\text{Å}$.

Liquids	Temp. (°C)	n	Max. Pressure (kbar)	Total No. of Fringes Shifted	Δn
n-hexane	25	1.3751	11.66	822	0.1566
n-pentane	30	1.3535	14.00	941	0.1809

Figure Captions

Figure 1: High Pressure Liquid Cell Interferometer: [1] stainless steel container, [2] stainless steel ring, [3] vitreous silica plano-convex lens, [4] vitreous silica spacer, [5] optical flat, [6] liquid under study, [7] polyethylene bag, [8] entrance hole, [9] O-rings, [10] stainless steel screw, [11] spring plunger, [12] stainless steel cap, [13] vitreous silica window, [14] teflon ring, and [15] stainless steel plate.

Figure 2: Schematic diagram of the experimental arrangement for measuring the variation of refractive index of liquids with pressure.

Figure 3: Variation of the refractive indices of n-pentane and n-hexane with pressure.

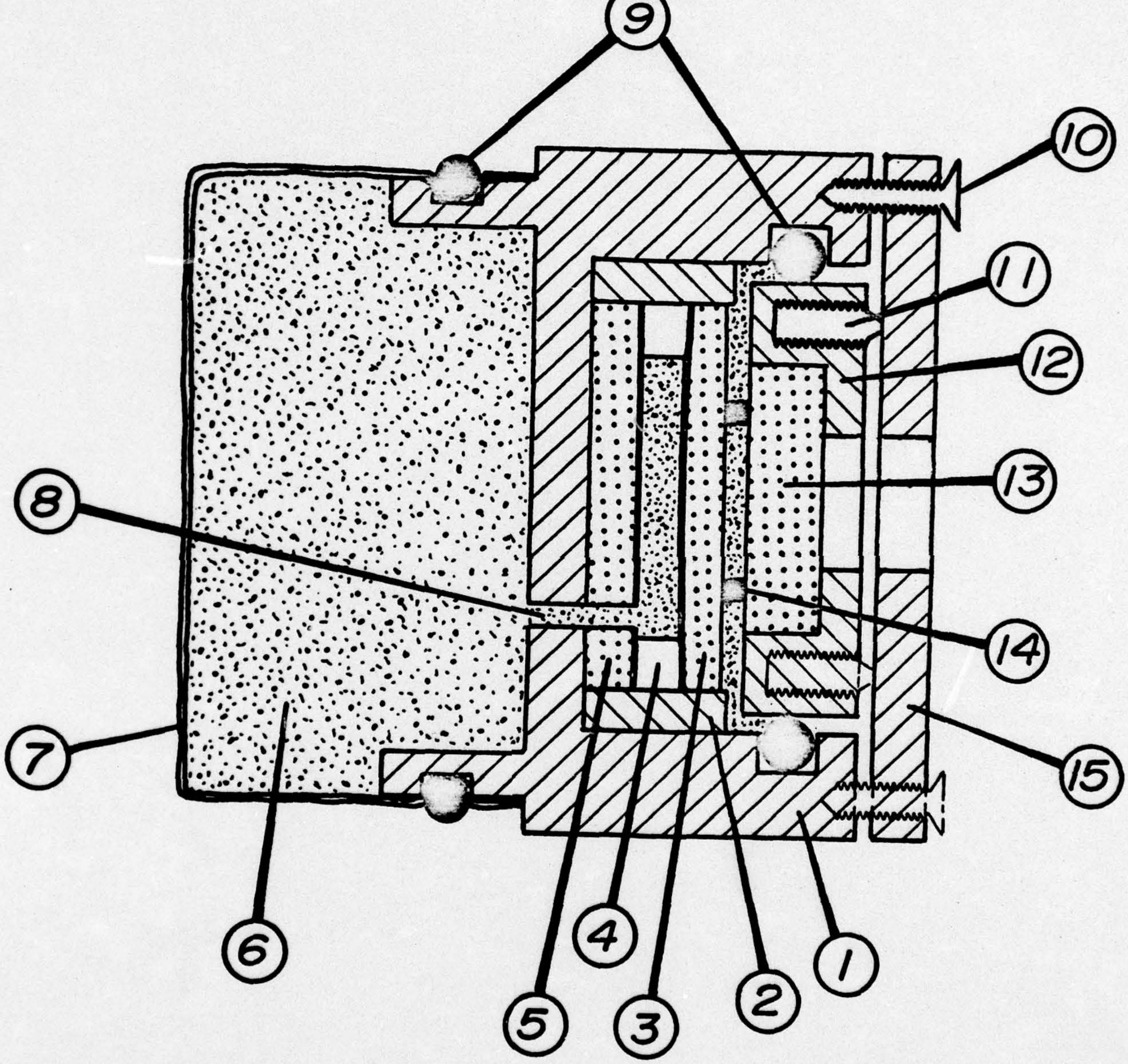

Figure 1

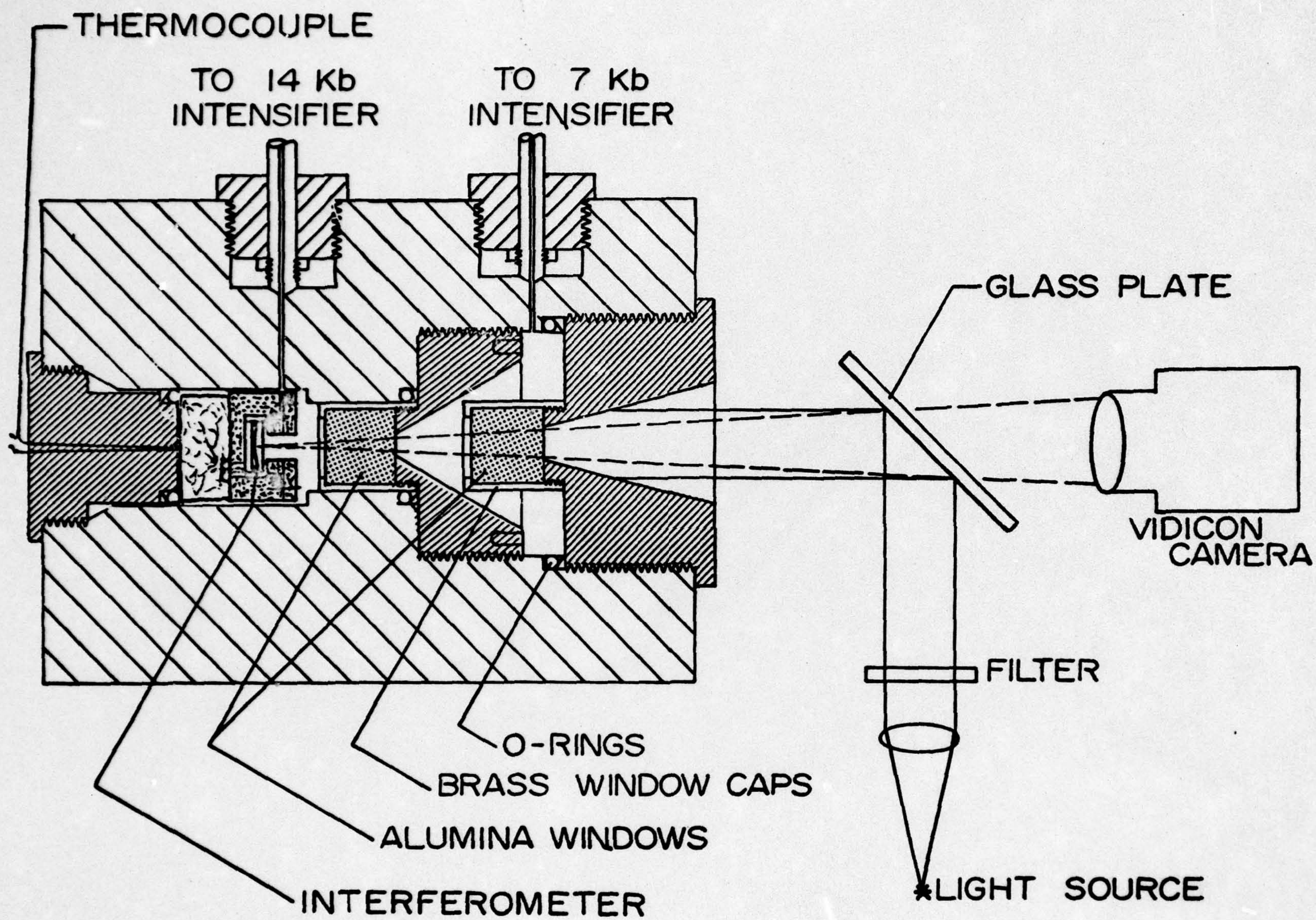
THERMOCOUPLE
TO 14 Kb INTENSIFIER
TO 7 Kb INTENSIFIER
GLASS PLATE
VIDICON CAMERA
FILTER
O-RINGS
BRASS WINDOW CAPS
ALUMINA WINDOWS
INTERFEROMETER
LIGHT SOURCE

Figure 2

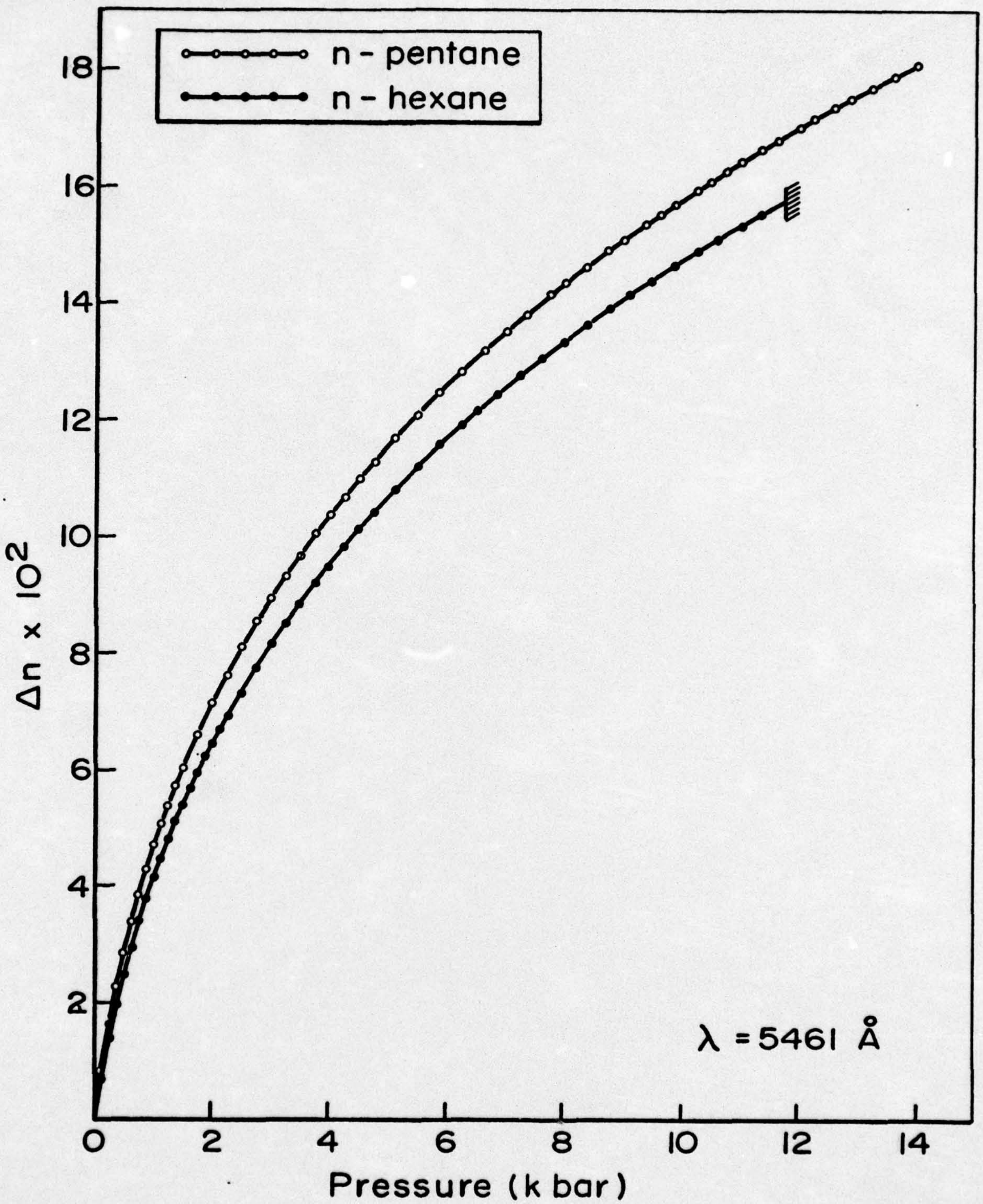
n - pentane
n - hexane
18
16
14
12
10
8
6
4
2
Δn x 10²
λ = 5461 Å
0
2
4
6
8
10
12
14
Pressure (k bar)

Figure 3

APPENDIX II

Submitted for publication in Physical Review Letters

Piezo-Optic Behavior and the Equation of State of Liquids

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ABSTRACT

Interferometric measurements on a number of liquids at high pressure (to 14 kbars) show (i) first experimental proof that the Eulerian frame-indifferent analogue strain E is a more useful strain measure than the Lagrangian strain, (ii) Keane's equation of state best describes each and all liquids studied, (iii) change in refractive index vs E is linear for all liquids, even though the volume strain involved is as high as 33%.

Consider the piezo-optic behavior of materials in their transparent region of spectrum. In the case of solids such as alkali-halides[1], α-quartz[2], vitreous silica[3] etc., the relationship between the change in refractive index Δn and pressure becomes slightly nonlinear at high pressures (say above 5 kbars), but the same data exhibit perfect linear relationship between Δn and the Lagrangian strain η in the entire range of pressures studied. In the case of liquids such as water and CCl_4, as mentioned in a previous article[4], Δn is grossly nonlinear with pressure, and Δn vs η is linear only at strains less than 2 or 3%. Motivated by the linearity of Δn vs η for the solids, one can view the nonlinearity of the Δn vs η for the liquids as possibly caused by (i) unreliable P-V data used to evaluate η, (ii) use of an inappropriate equation of state for the liquids when extrapolating and interpolating literature P-V data to cover our entire 14 kbar pressure range, (iii) nonapplicability of Lagrangian strain as a strain measure at our very high strains, and (iv) perhaps intrinsic nonlinearity of Δn with respect to all strain measures for liquids. Investigation into these possibilities

was made with high pressure interferometric measurements on a number of liquids under hydrostatic pressure and the results and conclusions are presented here.

Thomsen[5] and Davies[6,7] have recently reviewed the significance and properties of the various representation of strains, in particular the Lagrangian (η) and the Eulerian strain (ε). In brief, for the case of liquids under hydrostatic pressure, we have

$$\eta = \frac{1}{2}\left[\left(\frac{V}{V_o}\right)^{2/3} - 1\right] ;$$

$$\varepsilon = -\frac{1}{2}\left[\left(\frac{V_o}{V}\right)^{2/3} - 1\right] = \eta \left(\frac{V_o}{V}\right)^{2/3} .$$

where V_o and V are the initial and final specific volumes. As Truesdell and Noll[8] have shown, the Lagrangian or the "material" strain is rotationally invariant, i.e., invariant under changes of the frame of reference, whereas the Eulerian or "spatial" strain does not in general satisfy this invariancy criterion. Hence, to overcome this limitation of ε, Davies[6] has emphasized that the frame indifferent analogue, E, of the Eulerian strain ε should be used rather than ε. However, for the special case of isotropic bodies under hydrostatic pressure $E \equiv \varepsilon$ and the invariancy condition is trivially satisfied. Thus for the liquids in our hydrostatic pressure experiments, one can conveniently describe a frame-invariant strain at any pressure in either the Lagrangian representation or the Eulerian frame - indifferent analogue representation (which here is identically equal to Eulerian strain). These strains can be evaluated by using an appropriate equation of state to

extrapolate and interpolate experimental P-V data to cover our entire 14 kbar accessible pressure range.

The equations of state, for liquids and solids, that are widely used in the literature[9,10] contain two or three parameters; bulk modulus plus first and sometimes second pressure derivatives of the bulk modulus. Since these constants cannot always be obtained with high accuracy from even the best available data[9], they were evaluated for our studies by least squares fitting each equation of state to literature P-V data for each liquid. The standard error of estimate of each fitting was used as an indication of the ability of each equation of state to describe that particular liquid. In addition, where more than one source of P-V data was available for a liquid, the standard error was used to rank the reliability of each P-V data set.

Table I presents some of the experimental results obtained on a number of liquids by the high pressure interferometric method [4,11]. In every case except n-pentane the maximum pressures listed were determined by the freezing of the liquid at the stated temperature. It is found that the range of linearity between Δn and strain is much larger when using the strain E instead of η. This is true for each and all equations of state fitted to all P-V data of all the liquids studied. (Note that we will later show that three equations of state gave truly linear plots of Δn _vs_ E over the entire 14 kbar pressure range for all liquids studied). Figure 1 shows a representative graph of Δn _vs_ strain, for water evaluated from the P-V data of Adams[12] and the 2nd-Order Murnaghan equation of state. It is seen that Δn increases truly linearly with the strain parameter E for the entire stability field of water in the liquid phase, but that Δn _vs_ η is linear only below about 3% strain. Similar results were obtained with every liquid studied thus far.

An important result of this work is that we have experimentally shown for the first time that E is a more useful strain measure than the Lagrangian strain η. Identical conclusions for the usefulness of E over η were theoretically deduced by Davies[6] from both the ultrasonic data on the pressure dependence of the elastic moduli and the Hugoniot shock wave data for MgO.

Table II compares the fit of Δn for water to various degrees of polynomials in E for six of the widely used equations of state discussed in the literature. It is seen that a good linear relation between Δn and E is obtained with the Tait, 2nd-Order Murnaghan, 2nd-Order Birch, and Keane equations of state as evidenced by the value of the sum of the squares of the residuals as well as the standard error of estimate. The other equations, including those not listed there (such as Bridgman equation, etc.) yield poor linear fit and require higher order polynomials in E.

Similar analysis with the other liquids show that only three equations of state give a good linear relation of Δn with respect to E for <u>all</u> liquids. They are the 2nd-Order Murnaghan, 2nd-Order Birch, and the Keane equations of state. Anderson[13], and Chhabildas and Ruoff[14] have shown that of all the equations of state reported in the literature, only the Keane's equation yields physically as well as thermodynamically meaningful values on extrapolation to very high pressures. Hence the Keane equation is preferred over the other two that gave linear Δn <u>vs</u> E plots.

It is one of the more important results of our experiments that a single equation of state, Keane's equation, is found to give an excellent linear fit between Δn and E for <u>all</u> the liquids studied, irrespective of the nature of the liquid, whether polar or nonpolar and whether composed of spherically symmetric, or planar, or long chain molecules and even though the volume

strain involved is as high as 33%. Table II shows the linearity of Δn vs E calculated using the Keane equation of state.

Since one generally uses the same set of equations of state for both liquids and solids it is not unreasonable to expect the same general conclusions derived above for liquids to be valid for solids under hydrostatic pressure as well. The results on MgO[6] and NaCl[14] support this conjecture. Finally, the conclusions of the present investigation should be particularly useful now due to the renewed activities in the physics of condensed matter at high hydrostatic pressure with the development of diamond anvil high pressure system[15].

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Table I: Piezo-Optical Properties of Liquids.

Liquid	Temp. (°C)	λ in nm	n_o	Max. Pressure (kbar)	$\frac{\Delta V}{V_o}$ (%)	Total no. of Fringes Shifted	Δn_{max} ($n_{max} - n_o$)
water	25	546.1	1.3340	11.43	20.98	369	0.0842
CCl_4	25	546.1	1.4600	1.94	10.85	324	0.0671
n-decane	25	546.1	1.4114	3.23	14.37	402	0.0730
n-octane	25	546.1	1.3968	6.23	20.02	517	0.1116
n-heptane	25	546.1	1.3867	11.50	27.39	788	0.1507
n-hexane	25	546.1	1.3751	11.66	28.62	822	0.1566
n-pentane	30	546.1	1.3535	14.00	33.66	941	0.1809
chlorobenzene	25	589.3	1.5230	6.64	17.86	591	0.1188

Table II: Least-Squares Fitting Results for Water Using Adams P-V Data to Compute E; Δn Measured at 25°C Using λ589.3 nm.

Equation	$\Delta n = A + BE + CE^2$			Sum of Squares of Residuals	Standard Error
	A	B	C		
Tait	-2.50×10^{-4}	-0.990		4.43×10^{-7}	8.74×10^{-5}
	-2.69×10^{-4}	-0.991	-0.016	4.38×10^{-7}	8.77×10^{-5}
1st-Order Murnaghan	-1.06×10^{-4}	-0.987		7.54×10^{-7}	11.40×10^{-5}
	-0.07×10^{-4}	-0.980	-0.085	6.26×10^{-7}	10.48×10^{-5}
2nd-Order Murnaghan	-1.80×10^{-4}	-0.988		3.47×10^{-7}	7.74×10^{-5}
	-1.45×10^{-4}	-0.986	0.031	3.31×10^{-7}	7.62×10^{-5}
1st-Order Birch	-2.90×10^{-4}	-0.990		7.12×10^{-7}	11.08×10^{-5}
	-3.59×10^{-4}	-0.995	-0.058	6.53×10^{-7}	10.70×10^{-5}
2nd-Order Birch	-1.82×10^{-4}	-0.989		4.21×10^{-7}	8.52×10^{-5}
	-1.43×10^{-4}	-0.986	0.033	4.01×10^{-7}	8.39×10^{-5}
Keane	-1.85×10^{-4}	-0.989		4.44×10^{-7}	8.75×10^{-5}
	-1.48×10^{-4}	-0.986	0.032	4.26×10^{-7}	8.65×10^{-5}

Table III: Least-Squares Fitting Results of Δn at λ589.3 nm Using Keane's Equation.

Liquid	$\Delta n = A + BE + CE^2$			Sum of Squares of Residuals	Standard Error
	A	B	C		
Water	-1.85×10^{-4}	-0.989		4.44×10^{-7}	8.75×10^{-5}
	-1.48×10^{-4}	-0.986	0.032	4.26×10^{-7}	8.65×10^{-5}
CCl_4	-0.71×10^{-5}	-1.479		1.49×10^{-7}	6.35×10^{-5}
	-2.60×10^{-5}	-1.484	-0.155	1.38×10^{-7}	6.20×10^{-5}
n-Octane	2.13×10^{-4}	-1.325		1.26×10^{-6}	1.73×10^{-4}
	3.92×10^{-4}	-1.309	0.208	0.66×10^{-6}	1.35×10^{-4}
Chlorobenzene	-1.64×10^{-4}	-1.718		1.03×10^{-6}	1.60×10^{-4}
	1.05×10^{-4}	-1.693	0.359	0.21×10^{-6}	0.74×10^{-4}

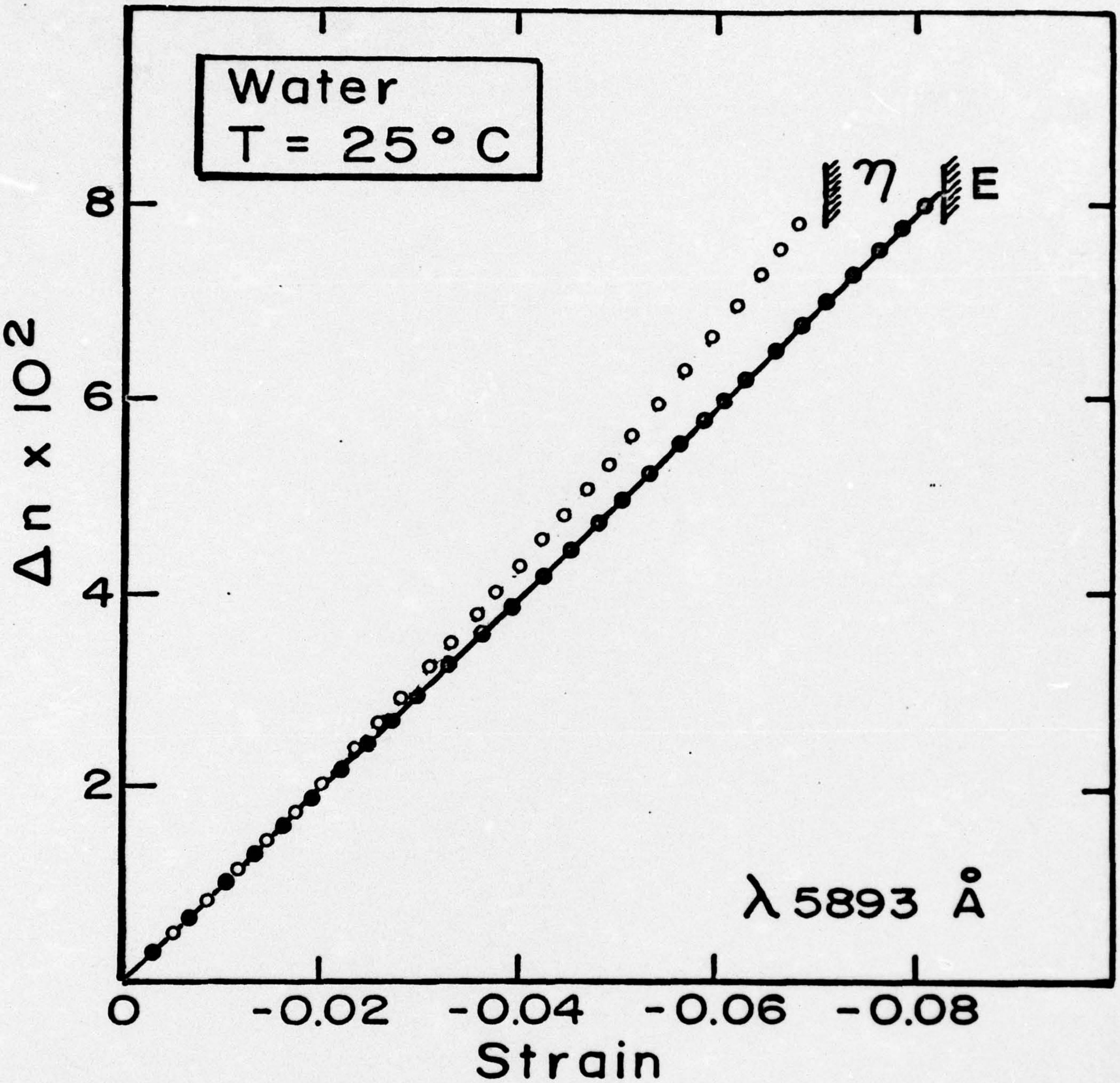

Fig. 1 Variation of refractive index of water with Lagrangian strain η, and strain parameter E.